

Fast pyrolysis of cork: Process modelling

Abstract

Waste cork streams consisting of Turkey oak (*Quercus cerris*), Birch (*Betula pendula*) and Ponytail palm (*Beaucarnea recurvata*) corks were studied to assess the possibility of valorization through pyrolysis. Kinetic parameters were determined using thermogravimetric analysis and multicomponent parallel reaction modelling using six pseudo component approximation and global kinetic modelling. Fast pyrolysis experiments were carried in bench scale modified fixed bed reactor and pilot scale twin-screw reactor.

Six pseudo component model fitted well to experimental results. Global kinetic models show that cork and phloem samples can be described by 5 pseudo components, i.e. humidity, hemicelluloses, cellulose, suberin and lignin. The activation energies of these pseudo components of *Q. cerris* cork varied 31-38 kJ/mol, 228-259 kJ/mol, 141-168 kJ/mol, 247-325 kJ/mol, and 130-307 kJ/mol respectively. The relative compositions estimated for these pseudo components in the different samples varied 0.04-0.05, 0.21-0.24, 0.16-0.19, 0.16-0.25, and 0.08-0.12 respectively.

Bench scale pyrolysis experiment resulted in low bio-oil yields indicating the importance of higher heat transfer during pyrolysis reactions. Pilot scale fast pyrolysis experiment of *Quercus cerris* phloem resulted with 52 % bio-oil yield of which 85% was organic fraction. Bio char yield was approximately 15%. Scanning electron microscopy analysis revealed that cellular structure of cork was retained after 500 °C bench scale experiments giving rise to a porous bio char. Overall, the results indicate that *Q. cerris* and other cork species as well as *Q. cerris* phloem have potential for conversion of bio-oil and bio chars through fast pyrolysis. Thus cork-rich tree barks can be valorized.

Keywords: Cork, kinetic modelling, first-order multi component model, fast pyrolysis, twin-screw reactor

1. Introduction

Cork is the outer bark of the cork oak (*Quercus suber* Linnaeus) tree. Cork is used principally in natural or technical cork stoppers production for wine bottles however, currently many different utilizations exist ranging from adsorbents to gaskets, etc (Pereira, 2011). Unconventional corks are obtained from tree barks that contain high amount of corks such as Turkey oak (*Quercus cerris* Linnaeus), birch (*Betula pendula* Roth), ponytail palm (*Beaucarnea recurvata* Lemaire), etc. These tree barks are often considered as waste streams and not commercially valorized (Şen et al. 2018). Thermal conversion methods such as fast pyrolysis have been increasingly used for valorization of waste biomass by converting it into bio-oils at high yields. Bio-oils are transported

easier than raw biomass and can be used without treatments or can be upgraded to produce drop-in fuels and chemicals.

Fast pyrolysis reactions occur in a very short interval of time, usually in a few seconds, at moderate temperatures. In these reactions heat and mass transfer, as well as reaction kinetics, are the most important factors that determine the product yields and selectivity (Bridgwater, 2012). Information on kinetic parameters, particularly on the activation energy is fundamental in designing new reactors, in simulation of fast pyrolysis process and in performing techno-economic analysis of the process.

The kinetic parameters can be obtained by application of solid state reaction kinetic analysis (Khawam and Flanagan, 2006). The kinetic analysis (isothermal or nonisothermal) is carried either by using curve-fitting methods or by using model-free (isoconversional) methods. Curve-fitting methods are more appropriate for modelling of thermal degradation of heterogeneous materials such as biomass where the total mass is assumed to be composed of different components (referred to as pseudo components) which degrade in overlapping course. First-order parallel reaction models are often used to describe biomass pyrolysis where information on kinetic parameters and biomass composition are obtained (Orfão et al. 1999, DiBlasi, 2008).

Bio-oils can be obtained at high yields by using finely ground and dry biomass reacted at temperatures approximately 500 °C in short vapor residence time. The fluid bed reactors are the most efficient reactors for this operation. However, it is also possible to use different reactor configurations to produce bio-oils and the byproduct bio chars (charcoal) (Bridgwater, 2012). The bio chars are valuable materials that can be used in soil amendment, heat production or in adsorption.

The aim of this study is to determine kinetic parameters of cork pyrolysis and to study the conversion of unconventional corks into bio-oils and chars by fast pyrolysis using a bench-scale reactor and pilot scale twin-screw reactor.

2. Materials and methods

2.1. Materials

Analyzed biomass types include Turkey oak (*Quercus cerris*) corks of 20-40, 40-60, and 60-80 mesh particle sizes, *Q. cerris* phloem of 40-60 mesh particle size, Ponytail palm (*Beaucarnea recurvata*) cork of 40-60 mesh particle size and birch (*Betula pendula*) cork of 40-60 mesh particle size.

2.2. Methods

2.2.1. Thermogravimetric analyses

A Perkin Elmer STA 6000 was used to carry thermogravimetric analysis (TGA) of biomass samples. In pyrolysis experiments a stepwise heating program was used. In the first step biomass samples were kept isothermally at 30 °C for 10 min., this step was followed by a heating step till 800 °C with heating rates varied between 5 to 200 °C/min. In the third step biomass samples are

kept isothermal for 10 min. at 800 °C. In the fourth step biomass samples were cooled with cooling rate of 50 °C/min. In all experiments nitrogen flow rate was set to 20 ml/min and alumina pans are used. Biomass weights were registered every 0.002 min time intervals.

2.2.2. Bench scale pyrolysis experiments

Two cylindrical glass reactors were designed (inner diameter and length of 3 cm and 26 cm, respectively) and built for bench scale pyrolysis experiments (Fig. 1). *Q. cerris* cork (60-80 mesh) was pyrolyzed at 500 °C using these reactors. In both experiments vapor residence time was kept short (a few seconds) and solid residence time was set to 1 h (in the first experiment solid fraction was retained isothermally during 1 h while in the second experiment the reactor was shut off immediately after introduction of biomass giving a decreasing temperature gradient during 1 h).

2.2.3. Pilot scale fast pyrolysis experiment

Pilot scale fast pyrolysis experiments were carried at Karlsruhe Institute of Technology (KIT) fast pyrolysis unit. A twin-screw reactor was used to pyrolyze ground *Q. cerris* cork and phloem fractions at 500 °C. The operational procedure was following:

The reactor length is 1.5 m, screw diameter is 4 cm. Biomass feed rate was 10 kg h⁻¹. Vapor residence time was less than 2 s. The carrier gas is Nitrogen. The mass ratio of biomass to heat carrier (steel balls) was 1:100. After the experiment two condensate fractions (organic-rich, and water-rich, respectively) were obtained at temperatures of 86 °C and 12 °C respectively as well as a bio char fraction (Kaltschmitt et al. 2009, Dahmen et al. 2012, Funke et al. 2016).

2.2.4. Pyrolysis products characterization

Pyrolysis experiments resulted in 3 products (bio char, bio-oil, gas products) or 4 products (bio char, bio-oil organic condensate, bio-oil aqueous condensate, gas products) after bench scale and pilot scale experiments respectively. Bio chars were characterized using elemental analysis and higher heating value tests. Bio-oil and gas products were characterized by gas chromatography (GC-FID) tests.

3. Results and discussion

3.1. Analysis of biomass thermograms

In all pyrolysis experiments cork samples started decomposing approximately at around 200 °C and a fast mass loss pattern is observed until 470 °C followed by a slow decomposition step (Fig. 2). In general, all six biomass types start decomposition at approximately 280 °C and 10-25% unconverted product or char was obtained. Mass loss curves shifted to higher temperatures with increasing heating rates, as expected.

3.2. Kinetic modelling

First-order parallel reaction modelling allowed good fits to experimental data. Four, five, and six pseudo component plus char models were developed. These models were tested using 40-60 mesh (0.25-0.42 mm) and 60-80 mesh (0.18-0.25 mm) *Q. cerris* cork particles at different heating

rates for their subsequent application in all biomass types. The results show that 4 and 5 pseudo component models fitted best with 40-60 mesh particles, while 6 pseudo component models fitted best with 60-80 mesh particles (Fig. 3) In the next step, using six pseudo component models, a global model, with fixed composition or allowing for composition variability, was developed to combine all modellings into one single global model. Activation energies for each pseudo components as well as biomass compositions were calculated by this way (Table 1, Table 2).

It is possible to tentatively assign identities to each pseudo component. Therefore, the first pseudo component is assigned to humidity. Its content is much lower in *Q. cerris* corks than other biomass types. Second and third pseudo components were assigned to hemicelluloses and cellulose. The higher activation energy pseudo component possibly corresponds to cellulose degradation. Their similar biomass ratio (close to 1) in corks supports this assumption. The fourth pseudo component is unclear. It may belong to overlapping decompositions of biomass components or extractives. The fifth pseudo component is assigned to suberin. Its relative composition is relatively higher in *Q. cerris* cork; it is present as a residual suberin in phloem and its content is lower in ponytail palm and birch corks. The last pseudo component is assigned to lignin. This is also supported by the amount of char since lignin contributes mainly to char formation (DiBlasi, 2008).

3.3. Fast pyrolysis results

The bench scale pyrolysis experiments resulted with approximately 6% liquid yield and 60% solid (bio char) yield. The gas yield was calculated by difference. The low liquid yield is related to insufficient heat transfer rate. The pilot scale pyrolysis experiments of phloem resulted with 52% liquid yield where approximately 85% was consisted of organic fraction (Fig. 4). Char yield varied between 14% and 17% (Table 3). As dry basis the bio-oil yield reduces to approximately 37% (Table 4). It can be concluded that the organic yield is comparably high given the high amount of ash contained in the feedstock. Operational problems occurred during cork pyrolysis during transport process of cork into the reactor.

3.4 Pyrolysis products characterization

The GC-FID analysis results show that the acetone fraction of bio-oil mainly consists of compounds that have less than 5 carbon atoms, while toluene fraction is composed of compounds that have 5 to 12 carbon atoms where 8 carbon compounds were the most abundant fraction (Fig. 5). The gas fraction of pyrolysis reaction consists mainly of less than 5 carbons. C6-C8 compounds were also detected to a lesser extent.

The SEM analysis showed that cork samples their cellular structure after 500 °C pyrolysis. Temperature gradient pyrolysis affected less the cellular structure of the produced bio-char than isothermal pyrolysis (Fig. 6).

4. Conclusions

The first-order parallel reaction model successfully predicted activation energies and cork chemical composition. By applying six component parallel reaction model and six heating rates

global and flexible composition models were developed with the former models, fitting were good (fit qualities were over 99%). The activation energies and biomass compositions were calculated for five pseudo components and char product. The results indicate that cork and phloem samples consist of 5 pseudo components, i.e. humidity, hemicelluloses, cellulose, suberin and lignin. The activation energies of the these pseudo components of *Q. cerris* cork varied 31-38 kJ/mol, 228-259 kJ/mol, 141-168 kJ/mol, 247-325 kJ/mol, and 130-307 kJ/mol respectively. The relative compositions of the pseudo components varied 0.04-0.05, 0.21-0.24, 0.16-0.19, 0.16-0.25, and 0.08-0.12 respectively. The char content varied between 9% and 23%.

The results of bench scale pyrolysis experiments showed that keeping vapor residence time alone was not sufficient to obtain high bio-oil yields. Higher heat transfer rates are necessary and fluid or spout bed reactor systems should be developed to achieve this objective.

The biochars obtained after 400 °C final pyrolysis temperature and temperature gradient fixed bed experiments were shown to retain their cellular structure indicating to be good alternatives for soil amendment treatments. The bio-oil composition showed compounds having six to twelve carbons which imply its utilization as gasoline alternative.

Technical problems were encountered in feeding cork samples into the twin-screw fast pyrolysis reactor. However, fast pyrolysis experiments of phloem samples resulted with approximately 52% bio-oil yields as received basis. This yield is in the expected range of bio-oil yields from forest wastes and reveals a promising result.

Overall, the results show that *Q. cerris* and other cork species as well as *Q. cerris* phloem have potential to be converted into bio-oil and biochar through fast pyrolysis. Thus cork-rich tree barks which are considered as waste streams, can be valorized.

5. References

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Tables

Table 1. Global kinetic modelling *Quercus cerris* corks

Pseudo components	<i>Q. cerris</i> cork 20-40 mesh		<i>Q. cerris</i> cork 40-60 mesh		<i>Q. cerris</i> cork 60-80 mesh	
	Ea (kJ/mol)	x	Ea (kJ/mol)	x	Ea (kJ/mol)	x
Ps 1	32.0	0.05	30.7	0.05	37.7	0.04
Ps 2	241.5	0.22	228.1	0.19	259.4	0.21
Ps 3	141.5	0.17	136.3	0.24	167.7	0.16
Ps 4	36.7	0	81.2	0.18	222.4	0.08
Ps 5	247.3	0.21	311.9	0.16	325.2	0.25
Ps 6	130.4	0.12	220.5	0.09	307.3	0.08
Char		0.23		0.09		0.18

Table 2. Global kinetic modelling *Quercus cerris* phloem, *Beaucarnea recurvata* cork, *Betula pendula* cork

Pseudo components	<i>Q. cerris</i> phloem 40-60 mesh		Ponytail palm cork 40-60 mesh		Birch cork 40-60 mesh	
	Ea (kJ/mol)	x	Ea (kJ/mol)	x	Ea (kJ/mol)	x
Ps 1	75.4	0.06	96.2	0.09	87.6	0.08
Ps 2	252.6	0.10	214.2	0.22	222.3	0.11
Ps 3	123.9	0.46	237.3	0.28	553.7	0.24
Ps 4	120.1	0.06	111.4	0.16	283.8	0.19
Ps 5	543.8	0.04	376.1	0.14	164.7	0.12
Ps 6	113.8	0.04	39.3	0	62.7	0.09
Char		0.24		0.11		0.17

Table 3. Results of the phloem fast pyrolysis yields as received basis

	Organic condensate (%)	Aqueous condensate (%)	Char (%)	Gas (%)	Deficit (%)
Experiment 1	41	7	14	21	17
Experiment 2	48	8	17	20	7

Table 4. Results of the phloem fast pyrolysis yields as dry basis

	Organic condensate (%)	Aqueous condensate (%)	Char (%)	Gas (%)	Deficit (%)
Experiment 1	29	4	16	23	28
Experiment 2	37	3	20	22	18

Figures

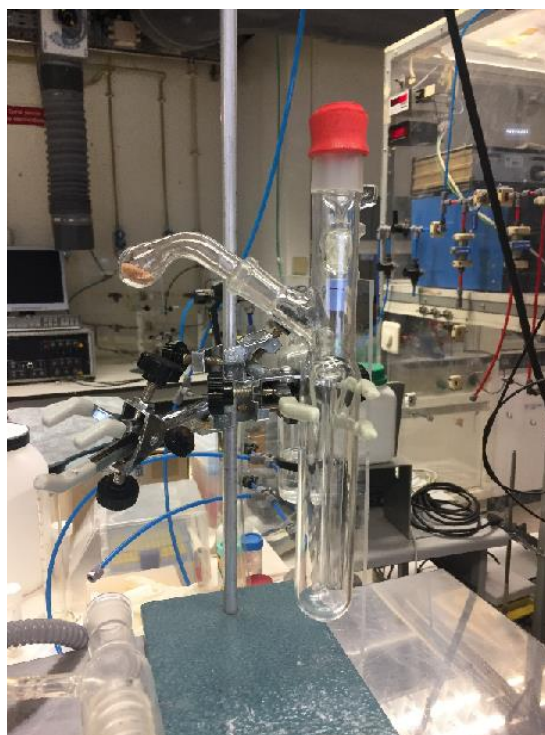


Figure 1. Bench scale glass reactor

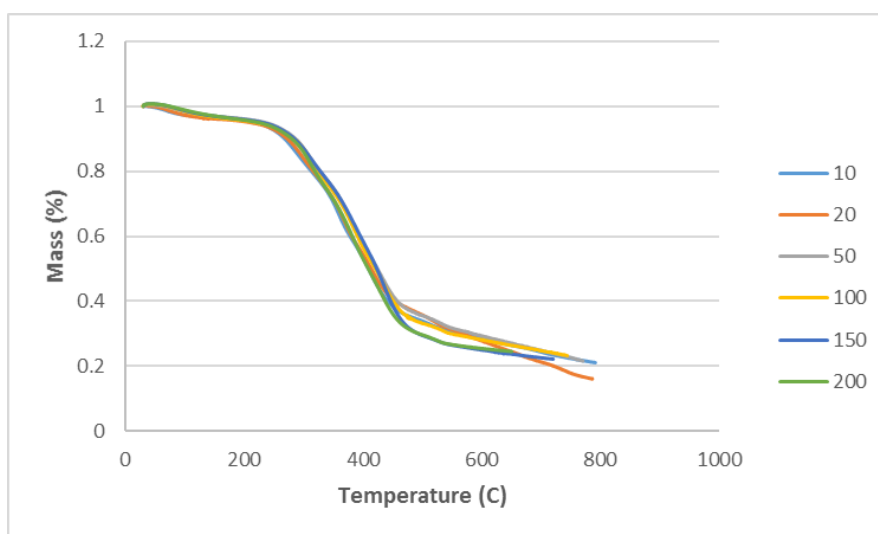


Figure 2. *Q. cerris* cork pyrolysis at different heating rates (°C/min) 20-40 mesh

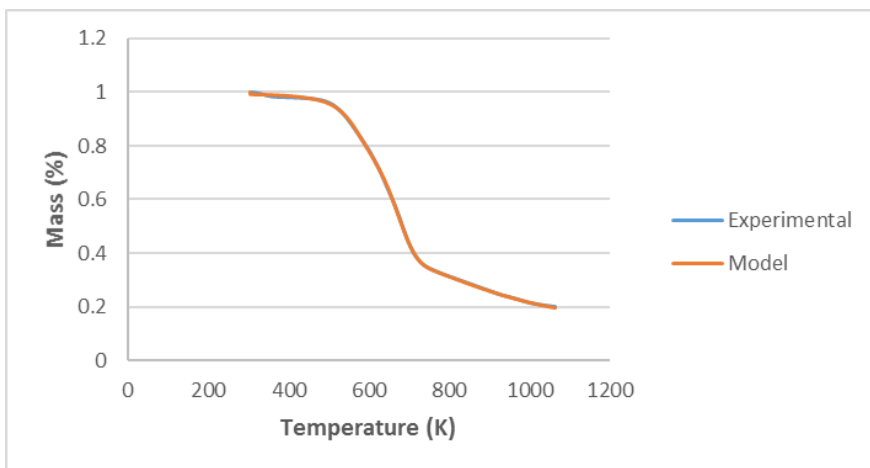


Figure 3. *Quercus cerris* cork six pseudo component model (60-80 mesh) 10 °C/min heating rate



Figure 4. *Quercus cerris* phloem bio-oil fractions

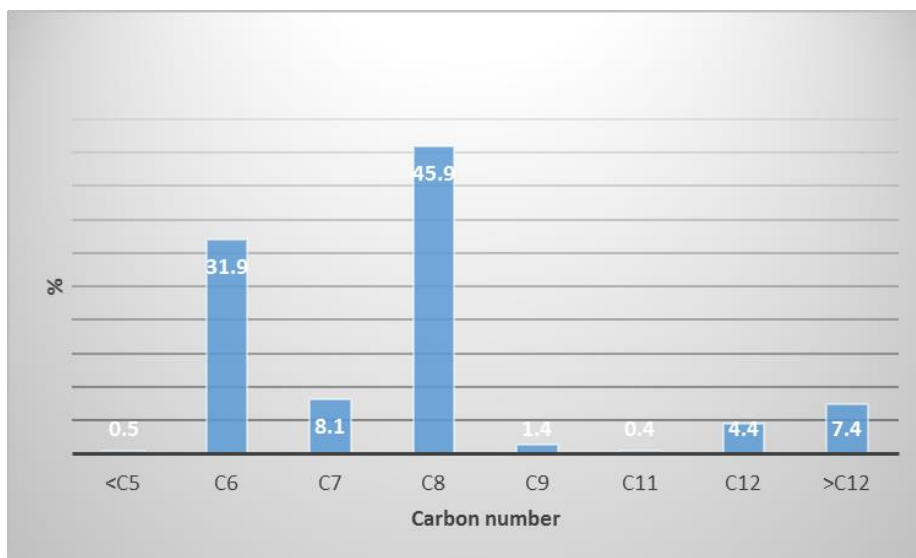


Figure 5. *Quercus cerris* cork bio-oil fractions obtained after bench scale pyrolysis

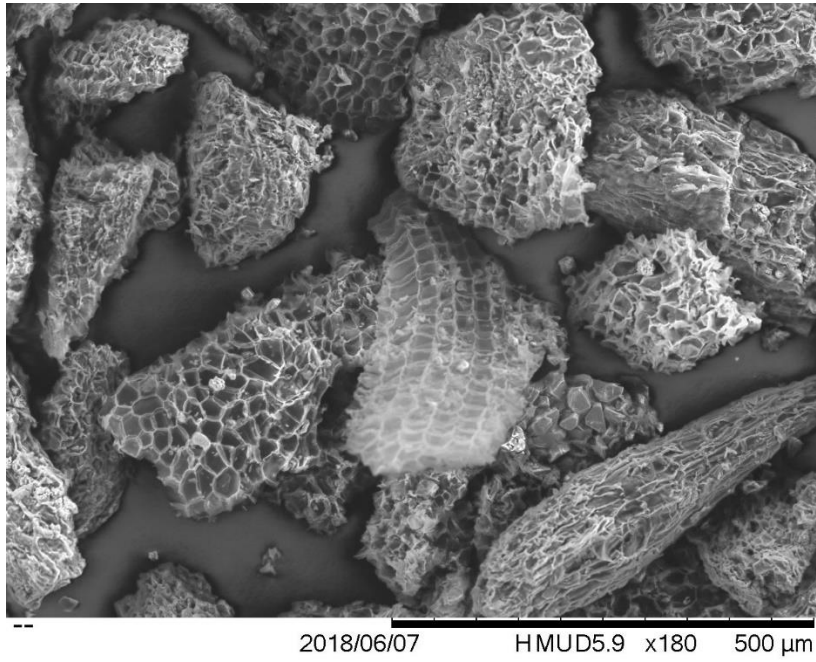


Figure 6. *Quercus cerris* cork bio char obtained after temperature gradient pyrolysis